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Preparation and Reactions of Samarium Diiodide in Nitriles.

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Abstract : *Samarium diiodide can be prepared from samarium metal in various nitriles. Because of its chemical inertness pivalonitrile is the most suitable solvent. Organic reactions mediated by SmI_2 are slower than in THF, but selectivities are often improved. Reactions are greatly accelerated by addition of catalytic amounts of some transition metal salts.* Copyright © 1996 Elsevier Science Ltd

Samarium diiodide is usually prepared from metallic samarium and 1,2-diiodoethane (or diiodomethane) in tetrahydrofuran[1]. There are a few cases where SmI_2 has been directly prepared in another solvent. We recently described the preparation and some reducing properties of this reagent in tetrahydropyran (THP)[2,3]. The use of SmI_2 in acetonitrile was first reported by Inanaga[5] and in 1992, Ishi and co-workers demonstrated that a Sm(II) species could be generated in this solvent by reaction of metallic samarium with trimethylsilyl halides[6].

Our attention was drawn to a paper where the preparation of SmI_2 in acetonitrile was reported. The reactivity of this reducing agent towards acid chlorides and acetophenone was also investigated and found to be quite different from our previous observations in THF[7]. Up to now, cyclic ethers (THF and THP) and acetonitrile are the only organic solvents where the preparation of SmI_2 from samarium metal has been performed[8]. For this reason we decided to investigate the preparation and reactivity of samarium diiodide in various nitriles.

We first focused on *acetonitrile* and were able to readily prepare SmI_2 in this solvent as previously described[7]. However, we were unable to isolate any of the α-ketols **3** (Table 1) under the conditions reported by Ruder[7], namely addition of acetophenone to a solution of SmI_2 in acetonitrile, immediately followed by dropwise addition of the acid chloride. In our hands the major product was the diol (entries 1, 2), resulting from the pinacolization of acetophenone, but also a complex mixture of products arising from reactions of the solvent was formed. In contrast it was possible to get α-ketols **3**, though in modest yields (30 %), from addition of a mixture of ketone (acetophenone or 2-butanone) and acid chloride to a solution of SmI_2 (Barbier conditions). Very small amounts of the symmetrical α-diketone generated from coupling of the acid chloride were also formed.

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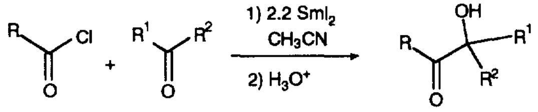
Table 1 : **Cross Coupling between Acid Chlorides and Ketones mediated by SmI_2 in Acetonitrile.**

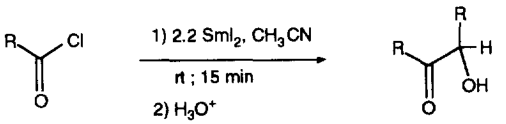


1 2 3

Entry[a]	R	R^1	R^2	3 : isolated yield %
1	n-C_8H_{17}	CH_3	C_6H_5	0 [b,c,d]
2	Cyclohexyl	CH_3	C_6H_5	0 [b,c]
3	Cyclohexyl	CH_3	C_6H_5	20 [e]
4	Cyclohexyl	CH_3	C_2H_5	25 [e]
5	n-C_8H_{17}	CH_3	C_2H_5	30 [f]
6	$C_6H_5OCH_2$	CH_3	C_2H_5	4 [g]
7	Cyclohexyl	H	C_2H_5	0 [e]

a) 20°C ; 15 min. ; a 1:1 mixture of acid chloride and ketone is added to SmI_2, unless otherwise stated. b) Ketone is added first, acid chloride is then added dropwise according to procedure described in ref. 7. c) Main product : pinacol of acetophenone. d) Same result in the presence of metallic samarium. e) By-products : $C_6H_{11}CO(CHOH)C_6H_{11}$, $C_6H_{11}COCOC_6H_{11}$, $C_6H_{11}COCOCH_3$, compounds arising from reactions of CH_3CN. f) By-products : n-$C_8H_{17}COCH(OH)n$-C_8H_{17}, n-$C_8H_{17}CO(OCOn$-$C_8H_{17})n$-C_8H_{17}, compounds arising from reactions of CH_3CN. g) Main products : phenol, $C_6H_5OCOCH_2OC_6H_5$.

Acid chlorides themselves (cyclohexanoyl chloride and *n*-nonanoyl chloride) are readily coupled by SmI_2 in acetonitrile into α-ketols **4** (Scheme 1), the corresponding α-diketones only being formed in small amounts (10 %). Under the same procedure, phenoxy acetyl chloride immediately decarbonylates with phenol as the main product.



4

R = cyclohexyl ; yield = 70 %

R = n-C_8H_{17} ; yield = 85 %

Scheme 1

To conclude, we were unable to reproduce the results of Ruder[7] concerning the cross-coupling of acid chlorides and acetophenone. We found that the reactivity of SmI_2 in acetonitrile towards acid chlorides or mixtures of acid chlorides and ketones is roughly the same as in THF. Unfortunately, many by-products are often formed, presumably because of the acidity displayed by the methyl group of acetonitrile under anionic conditions[10].

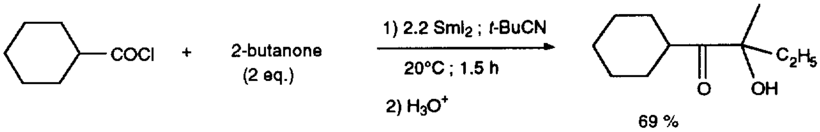
In order to overcome this problem we tested other nitriles as organic solvent for the preparation of SmI_2.

We found that SmI_2 could be quantitatively generated from reaction of metallic samarium and 1,2-diiodoethane in *propanenitrile*, *octanenitrile* and *pivalonitrile*. The experimental conditions are similar to those used in the preparation of SmI_2 in acetonitrile (see experimental part). In order to avoid the presence of metallic samarium in further experiments, 1:1 ratio of samarium to 1,2-diiodoethane was used. In these solvents, oxidation of Sm(II) to Sm(III) resulted in the solution changing from dark green to light brown.

We focused on the use of *pivalonitrile* because of the absence of acidic hydrogens and the low reactivity of the hindered nitrile group. Furthermore, pivalonitrile is easily removed in the work-up. Interestingly, samarium diiodide complexed with pivalonitrile has been previously prepared from samarium diiodide in THF through exchange of solvent and its solid-state structure has been established by crystal X-ray diffraction analysis[11]. In the crystal, the SmI_2 molecules are arranged in a bridging iodide polymeric structure, two pivalonitrile molecules being *N*-bonded to each samarium atom.

Samarium diiodide in pivalonitrile is less prone to mediate Barbier reactions than in THF (Table 2) : iodododecane is unreactive (entry 1) and allylic or benzylic halides need several hours at room temperature to go to completion instead of a few minutes in THF [12]. However the regioselectivity is much higher in pivalonitrile than in THF in the case of Barbier reactions involving allylic halides. In THF there is no regioselectivity, whereas in pivalonitrile one regioisomer is preferentially or even exclusively obtained (entries 5, 6, 7, 9, 10, 11), except in the case of cinnamylbromide the unbranched regioisomer predominates.

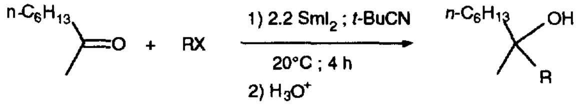
Cross-coupling between cyclohexanoyl chloride and butanone (nucleophilic acylation) mediated by SmI_2 in pivalonitrile gives α-ketol in good yield (Scheme 2), in contrast to the reaction in acetonitrile.



Scheme 2

Reactions are slower in pivalonitrile than in THF and surprisingly HMPA does not enhance the reactivity of samarium diiodide in nitriles (Barbier reactions or pinacolization of ketones). Because of the slugginess of many of the above reactions in pivalonitrile as compared to THF, we tried to use the beneficial effect of catalytic amounts of some transition metal salts for the acceleration of reactions promoted by SmI_2 in THF[1,13].

Table 2. : Barbier Reactions of Organic Halides with 2-octanone.



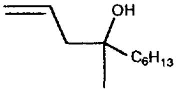
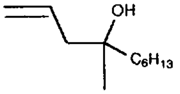
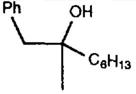
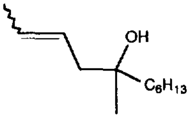
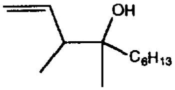
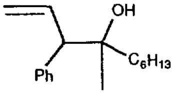
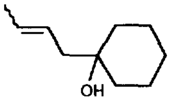
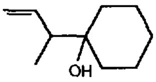
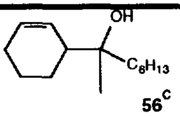
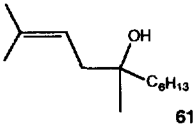
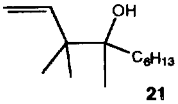
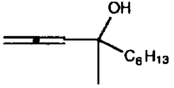
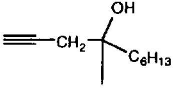
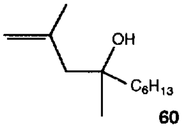
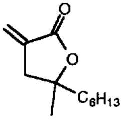
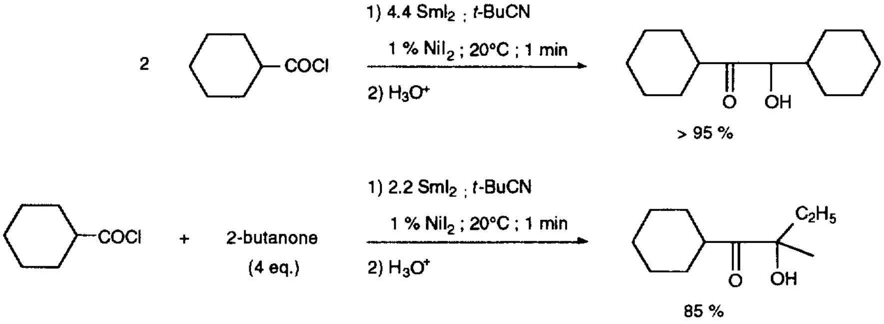
Entry	**RX**	**Products**: isolated yield % [a]
1	1- iodododecane	0 [b]
2	1-bromopropene	 **80**
3	1-iodopropene	 **65**
4	benzylbromide	 **65**
5	1-bromo-2-butene	 **60**  **4** [c]
6	cinnamylbromide	 **75** [c]
7 [d]	1-bromo-2-butene	 **53**  **9**
8	3-bromocyclohexene	 **56** [c]
9	4-bromo-2-methyl-2-butene	 **61**  **21**

Table 2. : **Barbier Reactions of Organic Halides with 2-octanone** (continued).

Entry	**RX**	**Products**: isolated yield % [a]
10	propargylbromide	 32  18
11	3-bromo-2-methylpropene	 60
12	methyl 2-(bromomethyl)acrylate	 63^{e}

a) Purification of crude materials by flash chromatography results in some degradation of the alcohols. b) Dodecane (10 %) . c) Mixture of diastereomers. d) Cyclohexanone. instead of 2-octanone. e) After chromatographies the product remains contaminated with small amounts of products arising from self coupling of the bromoester.

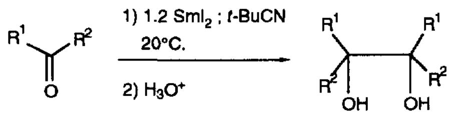
Indeed addition of small quantities of transition metal salts (1 % with respect to SmI_2) greatly reduces reaction times. Couplings involving acid chlorides go to completion within 1 min in the presence of nickel diiodide instead of 15 min (Scheme 3).



Scheme 3

The pinacolizations of ketones are also strongly accelerated either by iron acetylacetonate or by nickel halides (Table 3).

Table 3 : Pinacolization of Ketones.

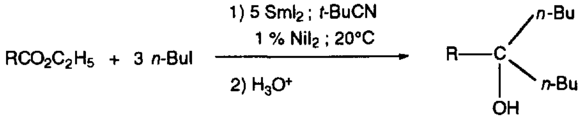


5

Entry	Ketone	Time (h)	5 : isolated yield %
1	2-octanone	24	11[a]
2	2-octanone	0.2	80 [a,b]
3	cyclohexanone	24	0 [c]
4	cyclohexanone	24	50[d]
5	cyclohexanone	2.5	78 [e]
6	cyclohexanone	0.5	77 [b]
7	cyclohexanone	0.2	90 [f]
8	cyclopentanone	2.5	85 [e]
9	cyclobutanone	2.5	90 [e]
10	acetophenone	0.1	94 [f,g]

a) *dl/meso* = 50/50. b) 1 % NiI_2. c) Small amount of crotonisation product. d) 60°C. e) 1 % $Fe(acac)_3$.
f) 1 % $NiBr_2(P(C_6H_5)_3)_2$. g) *dl/meso* = 79/21.

The Barbier reactions between esters and iodoalkanes are very slow in THF [1] and do not proceed at all in nitriles. Addition of nickel diiodide to a mixture of ester and 1-iodobutane rapidly gives tertiary alcohols in less than 30 min in a quantitative yield (Scheme 4)[14].



R = C_6H_5 ; 5 min : yield = 87 %

R = *n*-C_7H_{15} ; 30 min : yield = 94 %

Scheme 4

In conclusion samarium diiodide can be generated in various nitriles in quantitative yield. Pivalonitrile because of its chemical inertness seems to be the best solvent for organic transformations mediated by SmI_2, (for example acid chlorides give no by-products in nucleophilic acylation of ketones). Reactions are slower in this solvent but in some cases more selective, for example many homoallylic alcohols are produced regioselectively from substituted allylic halides. They can be greatly accelerated by addition of small quantities of transition metal salts. Studies concerning the scope of the organic transformations promoted by samarium (II) compounds in various nitriles, especially in pivalonitrile, are currently in progress.

EXPERIMENTAL

General: ^{1}H NMR and ^{13}C spectra were recorded at 250 MHz and 63 MHz respectively on a Bruker AM 250 instrument (unless otherwise stated). Chemical shifts are reported in part per million (δ) downfield from TMS. Coupling constants are reported in Hz. Infrared (IR) spectra were recorded neat on a Perkin-Elmer 257 and are reported in cm^{-1}.

Mass spectra (MS) data were determined on a GC/MS Ribermag R10-10 instrument. Chemical ionisation (CI) was carried out using NH_3 as the reactant gas and electronic impact was performed with 70 eV. Flash chromatographies were performed on silica gel (Merck 230-240 mesh; 0.0040-0.0630 mm).

All organic compounds were commercially available and distilled before use. Samarium powder (40 mesh) was purchased from Labelcomat Company. Nitriles were distilled under argon from calcium hydride (CaH_2).

All the reactions were carried out under argon in Schlenk tubes using standard vacuum line techniques.

Preparation of SmI_2 in nitriles. To a mixture of samarium powder (601 mg, 4.00 mmol) and 1,2-diiodoethane (1.127 g, 4.00 mmol) under argon at rt was added nitrile (4.00 mL) with vigorous stirring. After a short induction period a slightly exothermic reaction took place and the mixture turned dark green. After 8 h at rt, a slurry of SmI_2 was obtained. For pivalonitrile and octanenitrile heating at 40°C was needed to consume all the samarium metal.

Complexometric, argentimetric and iodine titrations[1b] were in agreement with quantitative formation of samarium diiodide.

Procedure for Barbier reactions with allylic and benzylic halides in pivalonitrile: In a Schlenk tube under argon, a suspension of SmI_2 in 4 mL of nitrile (4 mmol) and 1.8 mmol of halide and ketone in 3 mL of nitrile were mixed and stirred at rt. The mixture turned light green within a reaction time of 1 to 4 hours. It was then quenched with HCl (0.1 M) to obtain a clear solution and extracted with ether. The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over $MgSO_4$. After removal of solvent the crude material was purified by flash chromatography on silica gel (ethyl acetate/pentane 1:9 or ether/pentane 1:9).

Procedure for reactions with acid chlorides in pivalonitrile: In a Schlenk tube under argon, a suspension of SmI_2 in 4 mL of nitrile (4 mmol), 0.04 mmol of NiI_2 and 1.8 mmol of acid chloride (or 1.8 mmol of acid chloride and 7.2 mmol of ketone) in 3 mL of nitrile were mixed and stirred at rt. The mixture turned brown within 1 min. The work-up and purification were performed as described above. A similar procedure is used for reactions of esters (0.8 mmol) with 1-iodobutane (2.4 mmol) mediated by SmI_2 (4 mmol) in the presence of NiI_2 (0.04 mmol).

Procedure for pinacolisation of ketones in pivalonitrile: In a Schlenk tube under argon, a suspension of SmI_2 in 4 mL of nitrile (4 mmol), 0.04 mmol of transition metal complex and 3.3 mmol of ketone in 3 mL of nitrile were mixed and stirred at rt. After the mixture has turned brown, the work-up and purification were performed as described above.

4-methyl-1-decen-4-ol: Yield: 65%, as yellow oil; IR ν_{max}: 3478 (OH), 2856, 1641, 1450, 1260, 953, 797; ^{1}H-NMR (250MHz, $CDCl_3$) δ: 5.79 (1H, ddt, J = 16.6, 10.7, 7.3 Hz), 5.01 (2H, m), 2.13 (2H, dd, J = 7.3, 1.4 Hz), 1.52-1.13 (10H, m), 1.07 (3H, s), 0.81 (3H, t, J = 6.8 Hz); ^{13}C (62.9MHz, $CDCl_3$) δ: 134.21, 118.31, 72.15, 46.29, 41.84, 31.84, 29.86, 26.66, 23.78, 22.62, 14.05 ; MS m/z: 155 (M^+-OH), 129 (M^+-C_3H_5), 85 (M^+-C_6H_{13}), 69 (100.00), 55, 43 ; CI/NH_3 m/z: 171 (MH^+), 188 (MNH_4^+); HRMS calcd for $C_{10}H_{19}O$ $(M\text{-}CH_3)^+$155.1436, found 155.1427.

1-phenyl-2-methyl-2-octanol: Yield: 65%, as yellow oil; IR ν_{max}: 3433 (OH), 2932, 1453, 1133, 1094, 929, 700; ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.12 (5H, m), 2.62 (2H, d, J = 3.6 Hz), 1.42-1.09 (10H, m), 1.01 (3H, s), 0.80 (3H, t, J = 6.3 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ: 137.54, 130.40, 127.90, 126.14, 72.35, 47.82, 41.67, 31.75, 29.72, 26.43, 23.82, 22.50, 13.94; MS m/z: 220 (M^+), 205 (M^+-CH_3), 135 (M^+-C_6H_{13}),129 (M^+-C_7H_7), 92 (100.00, $C_8H_{16}O$), 69, 43 ; CI/NH_3 m/z: 221 (MH^+), 238 (MNH_4^+).
Anal Calcd for $C_{15}H_{24}O$ (220.35): C: 81.76, H: 10.98; Found : C: 81.80, H: 10.95.

5-methyl-2-undecen-5-ol: Yield: 60%, as yellow oil; IR ν_{max}: 3389 (OH), 2859, 1639, 1459, 1377, 1139, 969, 796; ^{1}H NMR (250 MHz, $CDCl_3$) δ: major isomer: 5.43 (2H, m), 2.06 (2H, dd, J = 5.8, 1.4 Hz), 1.63 (3H, d, J = 4.9 Hz), 1.51-1.12 (10H, m), 1.06 (3H, s), 0.82 (3H, t, J = 6.8 Hz), minor isomer: 5.43 (2H, m), 2.12 (2H, dd, J = 5.8, 1.4 Hz), 1.57 (3H, d, J = 4.9 Hz), 1.51-1.12 (10H, m), 1.09 (3H, s), 0.82 (3H, t, J = 6.8 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ: major isomer: 129.79, 126.68, 72.63, 45.34, 42.19, 32.24, 30.27, 27.01, 24.28, 23.00, 18.52, 14.46, minor isomer : 127.68, 125.83, 77.61, 73.41, 48.16, 39.30, 27.05, 24.44, 24.22, 24.00, 23.57, 13.41; MS m/z: 169 (M^+-CH_3), 129 (M^+- C_4H_7), 99 (M^+-C_6H_{13}), 69, 55, 43 (100.00) ; CI/NH_3 m/z: 185 (MH^+), 202 (MNH_4^+).
Anal Calcd for $C_{12}H_{24}O$ (184.31): C: 78.2, H: 13.12 ; Found : C: 77.83, H: 13.06.

3-phenyl-4-methyl-1-decen-4-ol: Yield: 75%, as yellow oil; ^{1}H NMR (200MHz, $CDCl_3$) δ: 7.27 (5H, m), 6.33 (1H, ddd, J = 16.6, 9.8, 3.5 Hz), 5.16 (2H, m), 3.30 (1H, m), 1.62-1.19 (10H, m), 1.15 (3H, s), 1.06 (3H, s), 0.88 (3H, t, J = 6.8 Hz); ^{13}C (62.9 MHz,$CDCl_3$) δ: 141.73, 141.51, 138.38, 138.27, 129.74, 129.67, 128.73, 127.02, 117.97, 117.87, 74.46, 66.64, 60.75, 60.72, 40.77, 40.60, 32.33, 30.34, 30.30, 25.38, 25.06, 24.05, 23.98, 23.09, 14.55 ; MS m/z: 129 (M^+-C_9H_8), 118 (100.00, $C_8H_{16}O$), 91, 69, 55, 43 ; CI/NH_3 m/z :247 (MH^+), 264 (MNH_4^+).
Anal Calcd for $C_{17}H_{26}O$ (246.39): C: 82.87, H: 10.63; Found: C: 82.85, H: 10.61.

1-(2'-butenyl) cyclohexanol: Yield: 53%, as yellow oil; IR ν_{max}: 3399 (OH), 2856, 1638, 1447, 1261, 850; ^{1}H NMR (250 MHz, $CDCl_3$) δ: major isomer : 5.43 (2H, m), 2.06 (2H, dd, J = 5.8, 1.4 Hz), 1.62 (3H, d, J = 4.4 Hz), 1.53-1.12 (10H, m), minor isomer : 5.43 (2H, m), 2.13 (2H, dd, J = 5.8, 1.4 Hz), 1.57 (3H, d, J = 4.4 Hz), 1.53-1.12 (10H, m); ^{13}C (62.9 MHz, $CDCl_3$) δ: major isomer: 129.21, 125.92, 70.94, 45.35, 37.26, 25.77,

22.13, 18.06, minor isomer : 127.20, 125.07, 71.70, 45.35, 37.17, 25.82, 21.75, 18.06; MS m/z: 121, 111, 99 (100.00, M^+-C_4H_7), 81, 55 ; CI/NH_3 m/z: 155 (MH^+), 172 (MNH_4^+).
Anal Calcd for $C_{10}H_{18}O$ (154.25): C: 77.87, H: 11.76 ; Found: C: 77.58, H: 11.79.

1-(1'-methyl-2'-propenyl)-cyclohexanol: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.75 (1H, m), 4.97 (2H, m), 2.13 (1H, m), 1.53-1.12 (10H, m), 0.94 (3H, d, J = 6.8 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ: 140.46, 115.62, 72.32, 34.83, 34.11, 18.06, 14.01, 12.96; MS m/z: 121, 111, 99 (100.00, M^+-C_4H_7), 81, 55 ; CI/NH_3 m/z: 155 (MH^+), 172 (MNH_4^+).
Anal Calcd for $C_{10}H_{18}O$ (154.25): C: 77.87, H: 11.76; Found: C: 77.80, H: 11.74.

2-(2'-cyclohexenyl)-2-octanol: Yield: 56%, as yellow oil; IR ν_{max}: 3438 (OH), 2932, 1646, 1464, 1375, 1203, 1153, 1061, 927, 760; ^{1}H NMR (250 MHz, $CDCl_3$) δ : 5.89-5.62 (2H, m), 2.29-2.14 (1H, m), 2.04-1.91 (2H, m), 1.90-1.69 (2H, m), 1.63-1.19 (10H, m), 1.16 and 1.09 (3H, s), 0.85 (3H, t, J = 6.3 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ: 129.82, 129.43, 127.62, 127.48, 74.55, 74.44, 45.26, 44.86, 40.51, 39.10, 31.94, 30.06, 30.01, 25.23, 25.21, 24.93, 24.50, 23.83, 23.56, 23.45, 23.40, 22.71, 22.42, 22.35, 14.14; MS m/z: 129 (M^+-C_6H_9), 81 (M^+-$C_8H_{17}O$), 69, 55, 43 (100.00) ; CI/NH_3 m/z: 211 (MH^+), 228 (MNH_4^+).
Anal Calcd for $C_{14}H_{26}O$ (210.35) : C: 79.94, H: 12.45; Found: C: 79.68 , H: 12.58.

2,5-dimethyl-2-undecen-5-ol: Yield: 61%, as yellow oil; IR ν_{max}: 3433 (OH), 2931, 1636, 1466, 1375, 1297, 1262, 1125, 1011; ^{1}H NMR (250MHz, $CDCl_3$) δ: 5.17 (1H, t, J = 7.8 Hz), 2.12 (2H, dd, J = 7.8, 1.4 Hz), 1.71 (3H, s), 1.60 (3H, s), 1.55-1.18 (10H, m), 1.11 (3H, s), 0.85 (3H, t, J = 6.8 Hz); ^{13}C (50.3 MHz, $CDCl_3$) δ: 145.57, 134.89, 73.08, 41.79, 40.20, 31.88, 29.92, 26.60, 26.08, 23.90, 22.03, 17.94, 14.07 ; MS m/z: 198 (M^+), 183 (M^+-CH_3), 181 (M^+-OH), 129 (M^+-C_5H_9), 113, 70 (100.00), 55, 43 ; CI/NH_3 m/z: 199 (M^+), 216 (MNH_4^+).
Anal Calcd for $C_{13}H_{26}O$ (198.34): C: 78.72, H: 13.21; Found: C: 78.65, H: 13.15.

3,3,4-trimethyl-1-decen-4-ol: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 6.05 (1H, dd, J = 16.6, 9.8 Hz), 5.08 (1H, dd, J = 9.8, 1.4 Hz), 5.03 (1H, dd, J = 16.6, 1.4 Hz), 1.91 (3H, s), 1.87 (3H, s), 1.55-1.18 (10H, m), 1.11 (3H, s), 0.85 (3H, t, J = 6.8 Hz); ^{13}C (50.3 MHz, $CDCl_3$) δ: 119.52, 113.12, 75.60, 40.21, 36.49, 31.89, 29.93, 26.08, 23.76, 22.63, 22.04, 20.95, 14.07; MS m/z: 198 (M^+), 183 (M^+-CH_3), 181 (M^+-OH), 129 (M^+-C_5H_9), 113, 70 (100.00), 55, 43 ; CI/NH_3 m/z: 199 (M^+), 216 (MNH_4^+).

4-methyl-1,2-decadien-4-ol: Yield: 32%, as yellow oil ; IR ν_{max}: 3374 (OH), 2932, 1958 (CH_2=C=CH), 1467, 1377, 1127, 922, 841 ; ^{1}H NMR (250MHz, $CDCl_3$) δ: 5.27 (1H, t, J = 6.3 Hz), 4.87 (2H, d, J = 6.3 Hz), 1.69-1.19 (10H, m), 1.16 (3H, s), 0.88 (3H, t, J = 6.3 Hz); ^{13}C (50.3 MHz, $CDCl_3$) δ: 205.64, 99.47, 78.41, 71.44, 42.95, 31.88, 29.72, 27.93, 24.15, 22.67, 14.14; MS m/z: 153 (M^+-CH_3), 129 (M^+-C_3H_3), 83 (M^+-C_6H_{13}), 69, 43 (100.00) ; CI/NH_3 m/z: 169 (MH^+), 186 (MNH_4^+).
Anal Calcd for $C_{11}H_{20}O$ (168.27): C: 78.51, H: 11.98; Found : C: 78.32, H: 11.84.

4-methyl-1-decyn-4-ol: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.57 (2H, d, J = 1.7 Hz), 2.41 (1H, J = 1.7 Hz), 1.65-1.20 (10H, m), 1.19 (3H, s), 0.88 (3H, t, J = 6.3 Hz); ^{13}C (50.3 MHz, $CDCl_3$) δ: 82.55, 71.43, 67.61, 41.25, 32.41, 29.79, 27.93, 22.73, 14.14; MS m/z: 153 (M^+-CH_3), 129 ($M^+-C_3H_3$), 83 ($M^+-C_6H_{13}$, 100), 69, 43 ; CI/NH_3 m/z: 169 (MH^+), 186 (MNH_4^+).

2,4-dimethyl-1-undecen-4-ol: Yield: 60%, as yellow oil ; IR ν_{max} (neat)/cm^{-1}: 3426 (OH), 2933, 1643, 1459, 1376, 1260, 1096, 889, 804 ; ^1H NMR (250 MHz, $CDCl_3$) δ : 4.83 (1H, d, J = 1.4 Hz), 4.66 (1H, d, J = 1.4 Hz), 2.11 (2H, d, J =3.9 Hz), 1.76 (3H, s), 1.39-1.11 (10H, m) 1.08 (3H, s), 0.81 (3H, t, J = 6.3 Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ: 142.76, 114.51, 72.23, 49.25, 42.5, 31.8, 29.81, 26.76, 24.86, 23.95, 22.55, 13.94 ; MS: m/z: 169 (M^+-CH_3), 129 (100.00, $M^+-C_4H_7$), 99 ($M^+-C_6H_{13}$), 69, 43 ; CI/NH_3 : m/z: 185 (MH^+), 202 (MNH_4^+). Anal Calcd for $C_{13}H_{26}O$ (184.31): C: 78.2, H: 13.12 ; Found: C: 78.15, H: 13.09.

4-hexenyl-4-methyl-2-methylene-4-butanolide: Yield: 63 %, as yellow oil; ^1H NMR (250 MHz, $CDCl_3$) δ: 6.16 (1H, s), 5.03 (1H, s), 2.12 (2H, s), 1.78-1.03 (13H, m), 0.88 (3H, t, J=6.8Hz); ^{13}C (62.9 MHz, $CDCl_3$) δ: 169.73, 135.91, 121.70, 83.63, 41.13, 39.22, 31.45,29.22, 26.31, 23.38, 22.32, 13.83.
MS: m/z 196 (M^+), 184 (M^+-CH_3), 111 ($M^+-C_3H_3$), ($M^+-C_6H_{13}$), 68, 43 ; CI/NH_3: m/z 197 (MH^+), 214 (MNH_4^+); HRMS calcd for $C_{11}H_{17}O$ $(M-CH_3)^+$181.1229, found 181.1229.

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